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The role of orbital products in the optimized effective potential method

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The orbital products of occupied and virtual orbitals are employed as an expansion basis for the charge density generating the local potential in the optimized effective potential method thus avoiding the use of auxiliary basis sets. The high computational cost arising from the quadratic increase of the dimension of this product basis with system size can be greatly reduced by elimination of the linearly dependent products according to a procedure suggested by Beebe and Linderberg [Int. J. Quantum Chem. **12**, 683 (1977)]. Numerical results from this approach show a very good agreement with those obtained from balancing the auxiliary basis for the expansion of the local potential with the orbital basis set. © 2008 American Institute of Physics.

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I. INTRODUCTION

In the field of molecular electronic structure methods, Kohn-Sham density functional theory¹ (KS-DFT) is widely used because it represents a very reasonable compromise between computational cost and accuracy of the results. From a historical perspective, one might distinguish three generations of density functionals: (a) the local density approximation² (LDA) based on the homogeneous electron gas, where the exchange-correlation energy is an explicit functional of the electron density; (b) the generalized gradient approximation³ (GGA) in which the gradient and higher derivatives of the density also appear in the representation of the exchange-correlation energy; and (c) orbital-dependent functionals which are implicit functionals of the density because the Kohn-Sham orbitals are uniquely determined by the ground state electron density as a consequence of the Hohenberg-Kohn theorem.⁴ The latter functionals may have the potential to overcome some of the shortcomings of LDA and GGA methods.⁵ They have the advantage that the major part of the exchange-correlation energy, i.e., the exchange energy, is known from Hartree-Fock (HF) theory in orbital-dependent form.

The determination of the local exchange-correlation potential from the variational principle is denoted as the optimized effective potential (OEP) method in the case of orbital-dependent functionals.^{6,7} Complications arise from the fact that, in contrast to LDA and GGA methods, the derivative of the exchange-correlation energy with respect to the density cannot be given explicitly. Instead, the variation of the electronic energy leads to an integral equation which has first been presented by Sharp and Horton⁶ and solved for atoms by Talman and Shadwick⁷ for the HF energy functional, i.e., the exchange-only case (OEPx). This pioneering work has been followed by an impressive number of articles discussing the OEP problem from various perspectives.^{8–28} Approximations to OEPx such as the method of Krieger-Li-

Iafrate (KLI),^{27,28} the local HF (LHF) method,²⁹ and the effective local potential³⁰ have also been reported.

In contrast to atoms, where the OEP equation can be solved numerically on a grid, an expansion of the orbitals in terms of an atomic orbital (AO) basis set, in general, cannot be avoided for molecules. The incompleteness of such a basis set raises important questions in the context of the OEP method which then relies on an appropriate representation of the response function. This function involves an infinite sum over virtual orbitals which has to be truncated in case of a finite basis set. The effect of this truncation on the eigenvalue spectrum of the response function has been discussed only recently.¹⁴ A convergence of the eigenvalue spectrum with increasing size of the AO basis set has been observed.¹⁴ If the basis set is sufficiently large, the addition of more basis functions only leads to additional eigenfunctions of the response function with very small eigenvalues. Since these eigenfunctions are eliminated in a singular value decomposition, the response function can then be considered as converged. However, rather large AO basis sets are needed to reach this point of convergence.¹⁴ A scheme for the construction of appropriate AO basis sets has been presented recently by Hesselmann *et al.*¹³ The first step in this scheme always involves a decontraction of the basis set which already leads to a considerable increase of its dimension.¹³ The high demands with respect to an appropriate choice of the AO basis set are not the only problem in the basis set OEP method. Since practical solutions of the OEP equation are mainly based on an expansion of the local potential in terms of an auxiliary basis,^{11,13,16,17,19,22} criteria for choosing this second basis set have to be found. It turned out that this is a very delicate problem because the auxiliary basis set needs to be carefully balanced with the AO basis set.¹³ A systematic solution to this problem has been given recently by Hesselmann *et al.*¹³ Regularization techniques can also be used to avoid the irregular oscillations in the potential arising from unbalanced basis sets.^{31,32}

The employment of an auxiliary basis can be avoided by using the products of occupied and virtual orbitals as an

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expansion basis for the local potential. This approach has first been used by Colle and Nesbet²¹ and discussed recently in great detail,¹⁴ but its usefulness with respect to practical calculations seems to be limited at first sight. Since the number of orbital products increases as N^2 if N is the number of AO basis functions, any matrix operation involving this product basis scales as N^6 . However, if it was possible to preselect an appropriate subset of the orbital products in such a way that the size of this subset increases only linearly with the system size, the unfavorable scaling behavior could be avoided thus making this approach amenable to practical applications. This will be the subject of the present contribution.

A general outline of the formalism in Sec. II will be followed by the results of numerical calculations for Ne and small molecules presented in Sec. III and compared to those obtained by Hesselmann *et al.*¹³ using balanced AO and auxiliary basis sets.

II. THE OEP EQUATIONS

In the OEP method, one seeks for a local potential $V_\sigma(\mathbf{r})$ such that the eigenfunctions $\psi_{p\sigma}$ of the one-electron Schrödinger equation,

$$\hat{F}_\sigma \psi_{p\sigma}(\mathbf{r}) = \varepsilon_{p\sigma} \psi_{p\sigma}(\mathbf{r}), \quad (1)$$

with the KS Hamiltonian,

$$\hat{F}_\sigma = -\frac{1}{2}\Delta + V_\sigma(\mathbf{r}), \quad (2)$$

minimize the total energy given by

$$\begin{aligned} E^{\text{OEP}}[\{\psi_{i\sigma}\}] = & \sum_\sigma \sum_i \int \psi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2}\Delta \right) \psi_{i\sigma}(\mathbf{r}) d^3\mathbf{r} \\ & + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d^3\mathbf{r} \\ & + \frac{1}{2} \int \rho(\mathbf{r}) \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \\ & + E_{\text{xc}}[\{\psi_{i\sigma}\}]. \end{aligned} \quad (3)$$

V_{ext} represents the external potential which is in general given by the Coulomb potential of the nuclei. $\rho(\mathbf{r}) = \sum_\sigma \sum_i |\psi_{i\sigma}(\mathbf{r})|^2$ is the electron density and $E_{\text{xc}}[\{\psi_{i\sigma}\}]$ is the orbital-dependent exchange-correlation energy. σ labels the two possible spin orientations α (spin up) and β (spin down). We use labels i, j, \dots for occupied orbitals, a, b, \dots for unoccupied orbitals, and p, q, \dots for general orbitals. The orbital-dependent exchange energy adopted from HF theory is given by

$$\begin{aligned} E_x[\{\psi_{i\sigma}\}] = & -\frac{1}{2} \sum_\sigma \sum_{i,j} \int \frac{\psi_{i\sigma}^*(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) \psi_{j\sigma}^*(\mathbf{r}') \psi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ & \times d^3\mathbf{r} d^3\mathbf{r}'. \end{aligned} \quad (4)$$

The KS potential in Eq. (1) can be split according to the second, third, and fourth energy contributions on the right-hand side of Eq. (3),

$$V_\sigma(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + V_\sigma^{\text{xc}}(\mathbf{r}). \quad (5)$$

$V_\sigma^{\text{xc}}(\mathbf{r})$ is the *local* exchange-correlation potential which is obtained as the functional derivative of the exchange-correlation energy with respect to the density in conventional KS-DFT. This is no longer possible if the exchange-correlation energy is orbital-dependent. Since there is a one-to-one mapping between the local potential in the KS equation [Eq. (1)] and the electron density, the variational condition can also be formulated via the derivative with respect to the local KS potential which can be obtained using the chain rule [see Eq. (17) below]. Expanding the local exchange-correlation potential as

$$V_\sigma^{\text{xc}}(\mathbf{r}) = \sum_k f_k(\mathbf{r}) \tilde{w}_{k\sigma}, \quad (6)$$

with¹¹

$$f_k(\mathbf{r}) = \int g_k(\mathbf{r}') \frac{1}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}', \quad (7)$$

the OEP problem is solved by minimization of the energy $E^{\text{OEP}}(\tilde{w}_{k\sigma})$ with respect to the expansion coefficients $\tilde{w}_{k\sigma}$ as suggested by Yang and Wu.^{22,31} Note that the functions g_k represent a set of square integrable functions, which is not the case for the functions f_k because the local KS potential is not necessarily square integrable.

In the OEPx, with the exchange energy being given by Eq. (4) and the correlation energy being completely neglected, one might wish to impose two constraints on the local exchange potential. The first constraint arises from the asymptotic $-1/r$ decay of this potential, which requires the charge density generating the potential to integrate to -1 . It can be seen from Eqs. (6) and (7) that this condition is fulfilled if the expansion coefficients $\tilde{w}_{k\sigma}$ obey the equation

$$\sum_k y_k \tilde{w}_{k\sigma} = -1, \quad (8)$$

with

$$y_k = \int g_k(\mathbf{r}) d^3\mathbf{r}. \quad (9)$$

A second constraint arises from the highest occupied molecular orbital (HOMO) condition according to which the energy ϵ_{HOMO} , as obtained from the one-electron Schrödinger equation [Eq. (1)] for the HOMO ψ_{HOMO} , should be identical to the expectation value $\langle \psi_{\text{HOMO}} | \hat{F}^{\text{HF}} | \psi_{\text{HOMO}} \rangle$ obtained with the HF operator \hat{F}^{HF} .^{27,33,34} This constraint can be written as

$$\int \psi_{\text{HOMO}\sigma}^*(\mathbf{r}) V_\sigma^{\text{xc}}(\mathbf{r}) \psi_{\text{HOMO}\sigma}(\mathbf{r}) d^3\mathbf{r} = \bar{\epsilon}_\sigma, \quad (10)$$

where the right-hand side is defined as

$$\begin{aligned}\bar{\epsilon}_\sigma &\equiv \int \frac{\delta E_{\text{xc}}[\{\psi_{j\sigma}\}]}{\delta \psi_{\text{HOMO}\sigma}(\mathbf{r})} \psi_{\text{HOMO}\sigma}(\mathbf{r}) d^3\mathbf{r} \\ &= \int \psi_{\text{HOMO}\sigma}^*(\mathbf{r}) \hat{V}_\sigma^{\text{xc, nl}} \psi_{\text{HOMO}\sigma}(\mathbf{r}) d^3\mathbf{r}.\end{aligned}\quad (11)$$

Defining the scalar product as

$$(f|g) \equiv \int d^3\mathbf{r} d^3\mathbf{r}' f(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} g(\mathbf{r}'), \quad (12)$$

and using Eqs. (6) and (7), the matrix element of the local exchange-correlation operator shown on the left-hand side of Eq. (10) can be written as

$$\begin{aligned}\int \psi_{\text{HOMO}\sigma}^*(\mathbf{r}) \hat{V}_\sigma^{\text{xc}}(\mathbf{r}) \psi_{\text{HOMO}\sigma}(\mathbf{r}) d^3\mathbf{r} \\ = \sum_k (|\psi_{\text{HOMO}\sigma}|^2 |g_k) \tilde{w}_{k\sigma}.\end{aligned}\quad (13)$$

Inserting Eq. (13) into Eq. (10), one finally obtains

$$\sum_k z_{k\sigma} \tilde{w}_{k\sigma} = \bar{\epsilon}_\sigma, \quad (14)$$

with

$$z_{k\sigma} = (|\psi_{\text{HOMO}\sigma}|^2 |g_k). \quad (15)$$

The constraints [Eqs. (8) and (14)] can be taken into account by using the Lagrangian multipliers leading to the variational condition

$$\frac{\partial}{\partial \tilde{w}_{k\sigma}} \left(E^{\text{OEP}} - \lambda_{1\sigma} \left(\sum_k y_k \tilde{w}_{k\sigma} + 1 \right) - \lambda_{2\sigma} \left(\sum_k z_{k\sigma} \tilde{w}_{k\sigma} - \bar{\epsilon}_\sigma \right) \right) = 0. \quad (16)$$

The derivative of the energy with respect to the expansion coefficients is obtained by the chain rule as^{22,31}

$$\begin{aligned}\frac{\partial E^{\text{OEP}}}{\partial \tilde{w}_{k\sigma}} &= \sum_i \int \frac{\delta E^{\text{OEP}}[\{\psi_{j\sigma}\}]}{\delta \psi_{i\sigma}(\mathbf{r}')} \frac{\delta \psi_{i\sigma}(\mathbf{r}')}{\delta V_\sigma(\mathbf{r})} \frac{\partial V_\sigma(\mathbf{r})}{\partial \tilde{w}_{k\sigma}} d^3\mathbf{r}' d^3\mathbf{r} \\ &+ \text{c.c.} = 0.\end{aligned}\quad (17)$$

The functional derivative of the orbitals with respect to the potential, occurring as the second term of the integrand in Eq. (17), is determined by using the perturbation theory for an infinitesimal perturbing potential δV_σ .

$$\frac{\delta \psi_{i\sigma}(\mathbf{r}')}{\delta V_\sigma(\mathbf{r})} = - \sum_{p(p \neq i)} \frac{\psi_{p\sigma}^*(\mathbf{r}) \psi_{p\sigma}(\mathbf{r}')}{\epsilon_{p\sigma} - \epsilon_{i\sigma}} \psi_{i\sigma}(\mathbf{r}). \quad (18)$$

From Eqs. (6) and (7), it can be seen that the derivative of the potential with respect to the expansion coefficients is given by

$$\frac{\partial V_\sigma(\mathbf{r})}{\partial \tilde{w}_{k\sigma}} = \int g_k(\mathbf{r}') \frac{1}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}'. \quad (19)$$

Defining the nonlocal operator $\hat{F}_\sigma^{\text{nl}}$ (the HF operator formed with the KS orbitals for OEPx) as

$$\frac{\delta E^{\text{OEP}}[\{\psi_{j\sigma}\}]}{\delta \psi_{i\sigma}(\mathbf{r}')} \equiv \hat{F}_\sigma^{\text{nl}} \psi_{i\sigma}^*(\mathbf{r}'), \quad (20)$$

inserting Eqs. (18)–(20) into Eq. (17), and using Eq. (12) yields

$$\begin{aligned}\frac{\partial E^{\text{OEP}}}{\partial \tilde{w}_{k\sigma}} &= \sum_{i \neq p} \int \psi_{i\sigma}^*(\mathbf{r}') \hat{F}_\sigma^{\text{nl}} \psi_{p\sigma}(\mathbf{r}') d^3\mathbf{r}' \frac{-1}{\epsilon_{p\sigma} - \epsilon_{i\sigma}} \\ &\times (g_k | \psi_{p\sigma}^* \psi_{i\sigma}) + \text{c.c.} = 0.\end{aligned}\quad (21)$$

Decomposing the double sum in Eq. (21) into two double sums according to $\sum_i \sum_{p(p \neq i)} \cdots = \sum_i \sum_{j(j \neq i)} \cdots + \sum_i \sum_a \cdots$ so that the first of these sums vanishes due to the opposite sign of the energy denominators, and using

$$\hat{F}_\sigma^{\text{nl}} = \hat{F}_\sigma + \hat{V}_\sigma^{\text{xc, nl}} - V_\sigma^{\text{xc}}(\mathbf{r}) \quad (22)$$

and the KS equation [Eq. (1)], Eq. (21) can be rewritten as

$$\begin{aligned}\frac{\partial E^{\text{OEP}}}{\partial \tilde{w}_{k\sigma}} &= \sum_{ia} \int \psi_{i\sigma}^*(\mathbf{r}') (V_\sigma^{\text{xc}}(\mathbf{r}') - \hat{V}_\sigma^{\text{xc, nl}}) \psi_{a\sigma}(\mathbf{r}') d^3\mathbf{r}' \\ &\times \frac{(g_k | \psi_{a\sigma}^* \psi_{i\sigma})}{\epsilon_{a\sigma} - \epsilon_{i\sigma}} + \text{c.c.} = 0.\end{aligned}\quad (23)$$

The nonlocal operator $\hat{V}_\sigma^{\text{xc, nl}}$ in Eq. (23) is given as

$$\frac{\delta E_{\text{xc}}[\{\psi_{j\sigma}\}]}{\delta \psi_{i\sigma}(\mathbf{r}')} \equiv \hat{V}_\sigma^{\text{xc, nl}} \psi_{i\sigma}^*(\mathbf{r}'). \quad (24)$$

From hereon we will drop the spin label σ and restrict ourselves to real orbitals. Using the expansion [Eq. (6)] with Eq. (7) in Eq. (23) and defining the matrix

$$M_{k,ia} \equiv \frac{(g_k | \psi_a \psi_i)}{\sqrt{\epsilon_a - \epsilon_i}}, \quad (25)$$

the gradient [Eq. (17)] of the energy with respect to the expansion coefficients can be written as

$$\nabla_{\tilde{\mathbf{w}}} E^{\text{OEP}} = 2\mathbf{M}\mathbf{M}^\dagger \tilde{\mathbf{w}} - 2\mathbf{M}\mathbf{w}^{\text{nl}}, \quad (26)$$

with the vector components of \mathbf{w}^{nl} being given by

$$w_{ia}^{\text{nl}} \equiv \frac{\int \psi_i(\mathbf{r}) \hat{V}^{\text{xc, nl}} \psi_a(\mathbf{r}) d^3\mathbf{r}'}{\sqrt{\epsilon_a - \epsilon_i}}. \quad (27)$$

Using Eq. (26), the variational condition [Eq. (16)] is obtained as

$$2\mathbf{M}\mathbf{M}^\dagger \tilde{\mathbf{w}} = 2\mathbf{M}\mathbf{w}^{\text{nl}} + \lambda_1 \mathbf{y} + \lambda_2 \tilde{\mathbf{z}}, \quad (28)$$

with

$$\tilde{z}_k = z_k + \sum_l \frac{\partial z_l}{\partial \tilde{w}_k} \tilde{w}_l - \frac{\partial \bar{\epsilon}}{\partial \tilde{w}_k}. \quad (29)$$

The second and third terms on the right-hand side of Eq. (29) arise from the dependence of the HOMO on the expansion coefficients. Neglecting these terms corresponds to the frozen orbital approximation which has been applied in the derivation of an approximate Newton method for the optimization of the expansion coefficients of the potential.³¹ Moreover, we found that the influence of the charge and HOMO constraints [Eqs. (8) and (14)] on the energy is very

small so that these conditions hardly restrict the variational freedom of the optimization procedure. Thus, the approximation $\tilde{\mathbf{z}} \approx \mathbf{z}$ can be safely applied because it results in a negligibly small increase of the total OEP energy. Equation (28) then represents a system of linear equations for the expansion coefficients \tilde{w}_{ia} . Before it can be solved the Lagrangian multipliers need to be determined. This can be done by multiplication of Eq. (28) with $\mathbf{y}^\dagger(\mathbf{M}\mathbf{M}^\dagger)^{-1}$ and $\mathbf{z}^\dagger(\mathbf{M}\mathbf{M}^\dagger)^{-1}$. Thus, the constraints [Eqs. (8) and (14)] result in a system of linear equations for the λ_i ,

$$\begin{aligned}\lambda_1 \mathbf{y}^\dagger(\mathbf{M}\mathbf{M}^\dagger)^{-1} \mathbf{y} + \lambda_2 \mathbf{y}^\dagger(\mathbf{M}\mathbf{M}^\dagger)^{-1} \mathbf{z} \\ = 2(-1 - \mathbf{y}^\dagger(\mathbf{M}\mathbf{M}^\dagger)^{-1} \mathbf{M} \mathbf{w}^{\text{nl}}), \\ \lambda_1 \mathbf{z}^\dagger(\mathbf{M}\mathbf{M}^\dagger)^{-1} \mathbf{y} + \lambda_2 \mathbf{z}^\dagger(\mathbf{M}\mathbf{M}^\dagger)^{-1} \mathbf{z} \\ = 2(\bar{\epsilon} - \mathbf{z}^\dagger(\mathbf{M}\mathbf{M}^\dagger)^{-1} \mathbf{M} \mathbf{w}^{\text{nl}}).\end{aligned}\quad (30)$$

If the matrix $\mathbf{M}\mathbf{M}^\dagger$ is singular or near-singular, its inverse cannot be directly obtained and one has to perform a singular value decomposition via a diagonalization of $\mathbf{M}\mathbf{M}^\dagger$ by a unitary transformation,

$$\mathbf{U}^\dagger \mathbf{M}\mathbf{M}^\dagger \mathbf{U} = \mathbf{D}. \quad (31)$$

The elements of the inverse matrix required for the solution of Eq. (28) and appearing in Eq. (30) are then obtained as

$$(\mathbf{M}\mathbf{M}^\dagger)^{-1}_{kl} = \sum_{\mu \in \{D_{\mu\mu} \neq 0\}} \frac{U_{k\mu}(U^\dagger)_{\mu l}}{D_{\mu\mu}}. \quad (32)$$

Note that the summation on the right-hand side of Eq. (32) excludes indices corresponding to zero eigenvalues $D_{\mu\mu} = 0$.

It is now a common practice to choose the expansion functions g_k for the potential as an auxiliary basis set of Gaussians.^{11,13,16,19,22} Such a basis set needs to be carefully balanced with the AO basis set to obtain meaningful OEP results.¹³ It should also span approximately the same space as the products $\psi_a(\mathbf{r})\psi_i(\mathbf{r})/\sqrt{\epsilon_a - \epsilon_i}$ because the response function projects any basis onto this space.¹⁶ It therefore seems natural to choose these products directly as an expansion basis,^{14,21} thus avoiding the use of auxiliary basis sets. The matrix \mathbf{M} represents simply the metric of the basis in this case. Since it is highly singular,¹⁴ only a small number of eigenfunctions with nonzero eigenvalues survive in a singular value decomposition.¹⁴ It would therefore greatly reduce the dimension of the matrix $\mathbf{M}\mathbf{M}^\dagger$ if it were possible to pre-select a relatively small set of linearly independent product functions. A procedure fulfilling this task has been developed by Beebe and Linderberg.³⁵ It is based on a Cholesky decomposition accompanied by a rearrangement of the basis vectors in each iteration cycle as described in the Appendix. Thus, the number of such iteration cycles is limited to the number of linearly independent products, which is much smaller than the total number of products (see below, Table IV).

Using the products $\psi_a(\mathbf{r})\psi_i(\mathbf{r})$ as an expansion basis, there is still another problem that needs to be resolved: these products integrate to zero thus making it impossible to fulfill the charge condition [Eq. (8)] because all integrals given in

Eq. (9) vanish. It is therefore necessary to supplement the expansion basis by one additional function $g(\mathbf{r})$ which is normalized such that

$$\int g(\mathbf{r}) d^3\mathbf{r} = 1. \quad (33)$$

Note that the coefficient of this function is constrained to -1 by the charge condition and does not need to be determined. In analogy to a procedure suggested by Yang and Wu,²² the corresponding contribution to the potential is separated by splitting the complete potential into two parts:

$$V^{\text{xc}}(\mathbf{r}) = V_0^{\text{xc}}(\mathbf{r}) + \Delta V^{\text{xc}}(\mathbf{r}), \quad (34)$$

with

$$V_0^{\text{xc}}(\mathbf{r}) = \sum_{ia} \int \frac{\psi_i(\mathbf{r}')\psi_a(\mathbf{r}')}{\sqrt{\epsilon_a - \epsilon_i}} \frac{1}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}' \tilde{w}_{ia}, \quad (35)$$

and

$$\Delta V^{\text{xc}}(\mathbf{r}) = - \int \frac{g(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}', \quad (36)$$

where only the contribution $V_0^{\text{xc}}(\mathbf{r})$ to the exchange-correlation potential has to be determined. Adding $\Delta V^{\text{xc}}(\mathbf{r})$ to the Hartree potential, i.e., the second term on the right-hand side of Eq. (5), results in a reference potential showing the correct asymptotic behavior. Note that the sum on the right-hand side of Eq. (35) includes only orbital products obtained according to the prescription given in the Appendix.

The function $g(\mathbf{r})$ still needs to be specified. A convenient choice is

$$g(\mathbf{r}) = \frac{1}{N} \rho(\mathbf{r}), \quad (37)$$

where $N = N_\alpha + N_\beta$ represents the total number of electrons. Inserting Eq. (37) into Eq. (36) and adding this contribution to the second term on the right-hand side of Eq. (5) lead to the Fermi-Amaldi potential.³⁶ Another possible choice is the charge density resulting from the HOMO,

$$g(\mathbf{r}) = |\psi_{\text{HOMO}}(\mathbf{r})|^2. \quad (38)$$

If Eq. (34) is inserted in Eq. (23), one may absorb the matrix elements of the known contribution ΔV^{xc} into the nonlocal part. This simply means that $V^{\text{xc}}(\mathbf{r})$ has to be replaced by $V_0^{\text{xc}}(\mathbf{r})$, and $\hat{V}^{\text{xc},\text{nl}}$ in Eq. (27) has to be replaced by $\hat{V}^{\text{xc},\text{nl}} - \Delta V^{\text{xc}}(\mathbf{r})$. Otherwise the development of the formalism remains unchanged except that the charge constraint is now automatically taken into account so that only the HOMO constraint has to be explicitly considered.

III. NUMERICAL RESULTS

The formalism described in the previous section has been implemented in the MOLPRO program package³⁷ for the exchange-only case. The basis sets used are aug-cc-pV6Z (Ref. 38) for Ne and d-aug-cc-pVTZ (Ref. 39) for the molecular calculations. These basis sets are decontracted and supplemented with additional primitive Gaussians as described by Hesselmann *et al.*¹³ We have also adopted the

TABLE I. Number N_v of linearly independent orbital products as selected by the Cholesky decomposition for Ne, H₂O, and CO. Results obtained from three different values of the threshold λ_{\min} for zero diagonal elements of the Cholesky matrix are shown. The total number N_p of orbital products is also given.

	N_v^a	N_v^b	N_v^c	N_p
Ne	13	16	19	47
H ₂ O	79	95	110	265
CO	96	113	137	404

^a $\lambda_{\min}=5 \times 10^{-5}$.

^b $\lambda_{\min}=10^{-5}$.

^c $\lambda_{\min}=10^{-6}$.

geometric data of the molecules from these authors which makes the results directly comparable.

It is important to choose the threshold λ_{\min} for vanishing diagonal elements L_{kk} of the Cholesky matrix given in the Appendix appropriately. A too large value restricts the variational freedom, and thus makes the total OEP energy larger than the variational minimum because the number of $\psi_a\psi_i$ products is then too small to represent a sufficiently flexible basis set for the expansion of the potential. Choosing a too small value leads to numerical instabilities resulting in a slowdown or even breakdown of the self-consistent iteration procedure. Moreover, the basis set for the expansion of the potential becomes unnecessarily large in this case. With respect to computational efficiency it is of course desirable to make the expansion basis as small as possible. The number of expansion functions for three different values of λ_{\min} as well as the total number of orbital products is shown in Table I. It can be seen that the vast majority of products must be considered as linearly dependent. A threshold of $\lambda_{\min}=10^{-5}$ proved to be a reasonable choice in our calculations. Increasing this value to 5×10^{-5} still gives acceptable results as can be seen from the tables presented in the following. Lowering the threshold from 10^{-5} to 10^{-6} does not lead to a significant

TABLE III. Difference between OEPx and HF total electronic energies in millihartree. Results from the present method are compared to those obtained by Hesselmann *et al.* (Ref. 13) using an expansion of the local exchange potential in a balanced auxiliary basis set. λ_{\min} is the threshold for zero diagonal elements in the Cholesky decomposition.

System	$E^{\text{OEPx}} - E^{\text{HF}^a}$	$E^{\text{OEPx}} - E^{\text{HF}^b}$	$E^{\text{OEPx}} - E^{\text{HF}^c}$
Ne	1.689	1.683	1.684
H ₂ O	2.335	2.318	2.532
CO	5.333	5.240	5.786
C ₂ H ₂	4.353	4.299	4.674

^aPresent work, $\lambda_{\min}=5 \times 10^{-5}$.

^bPresent work, $\lambda_{\min}=10^{-5}$.

^cHesselmann (Ref. 13).

change of the results, but a larger number of SCF iteration cycles indicates a decrease of numerical stability.

Another choice concerns the reference potential ΔV^{xc} [see Eq. (36)] that provides the correct long-range behavior of the potential. Considering the alternatives [Eqs. (37) and (38)], only a negligibly small difference in the numerical results has been observed. The numbers presented in the following have been obtained with Eq. (38).

The energies of the occupied molecular orbitals and the lowest unoccupied molecular orbital for Ne and H₂O, obtained with two different cutoff parameters for zero diagonal elements in the Cholesky decomposition, are given in Table II. These are compared to the molecular orbital (MO) energies obtained by Hesselmann *et al.*,¹³ which belong to the most reliable OEPx results for molecules reported up to now in the literature. In the case of Ne, the MO energies are also shown, calculated with the exact local exchange potential obtained from numerical calculations on a grid, as given by Hesselmann *et al.*¹³ The agreement with the present results is very good. The differences between the OEPx and HF total energies are shown in Table III. There is again a perfect

TABLE II. OEPx and HF orbital energies in a.u. for Ne and H₂O. Results from the present method are compared to those obtained by Hesselmann *et al.* (Ref. 13) using an expansion of the local exchange potential in a balanced auxiliary basis set. In the case of Ne, results obtained from the exact numerical exchange potential on a grid are also given. The designation of the orbitals in the second column indicates the irreducible representation of the corresponding point group. λ_{\min} is the threshold for zero diagonal elements in the Cholesky decomposition.

System	Orbital	OEPx ^a	OEPx ^b	OEPx ^c	OEPx ^d	HF
Ne	1s	-30.8197	-30.8201	-30.8201	-30.8200	-32.7724
	2s	-1.7181	-1.7181	-1.7181	-1.7181	-1.9304
	2p	-0.8507	-0.8507	-0.8507	-0.8507	-0.8504
	3s	-0.1903	-0.1907	-0.1904	-0.1922	0.0475
H ₂ O	1a ₁	-18.9729	-18.9738	-18.9722		-20.5664
	2a ₁	-1.1781	-1.1781	-1.1783		-1.3534
	1b ₂	-0.7122	-0.7122	-0.7127		-0.7178
	3a ₁	-0.5823	-0.5823	-0.5829		-0.5850
	1b ₁	-0.5092	-0.5092	-0.5091		-0.5103
	4a ₁	-0.2014	-0.1996	-0.1998		0.0068

^aPresent work, $\lambda_{\min}=5 \times 10^{-5}$.

^bPresent work, $\lambda_{\min}=10^{-5}$.

^cPotential expanded in an auxiliary basis set (Ref. 13).

^dNumerical potential on a grid (Ref. 13).

TABLE IV. Number N_v of linearly independent orbital products as selected by the Cholesky decomposition for the first four members of the polyynes series. The total number N_p of these products is also given.

	N_v^a	N_p
C ₂ H ₂	52	248
C ₄ H ₂	100	762
C ₆ H ₂	137	1554
C ₈ H ₂	172	2626

^a $\lambda_{\min} = 10^{-5}$.

agreement for Ne, whereas the present OEPx total energies for the molecules are slightly lower than those obtained by Hesselmann *et al.*¹³

It has already been mentioned that the usefulness of the present approach rests on a sufficiently small number of linearly independent orbital products $\psi_a\psi_i$ selected by the Cholesky decomposition described in the Appendix. This number should not only be much smaller than the total number of such products but should also increase only linearly with system size. We illustrate the scaling behavior by comparing the number of selected orbital products to the total number of such products for the first four members of the polyynes series C_{2n}H₂, with $n=1,2,3,4$. The results obtained with the aug-cc-pVTZ basis set and a threshold of 10^{-5} for the Cholesky decomposition are shown in Table IV. Note that only the orbital products, transforming as the completely symmetric irreducible representation of the point group $D_{\infty h}$, have been taken into account. It can be seen that the number of selected products needed for the expansion of the local potential grows much more slowly than the total number of such products. The numbers given suggest a near-linear increase as expected.

It has sometimes been stressed that OEPx and related approaches, such as the KLI (Refs. 27 and 28) and LHF (Ref. 29) methods, give more meaningful virtual orbitals than HF. This is a consequence of the fact that the HF operator is not self-interaction free for the virtual orbitals.⁴⁰ The occupied orbitals, on the other hand, are in general quite similar for both HF and OEPx. However, in some cases the OEPx method can also lead to a considerable improvement of the MO energy spectrum for the occupied orbitals. This can be illustrated by considering the N₂ molecule as the most prominent example. In this case even the ordering of the occupied MO's is changed as can be seen from Table V, which shows the MO energies for the occupied orbitals of N₂ as obtained from both HF and OEPx calculations with an N–N bond length of 2.0744 a.u. The HOMO has even the wrong symmetry ($1\pi_u$) in the case of HF. The OEPx calculation yields the $3\sigma_g$ orbital as the HOMO in accordance with the experimentally observed ionization potentials.⁴¹ The large energy difference of 0.05 a.u. between the HF and OEPx values for the $1\pi_u$ orbital is quite remarkable. That this difference arises mainly from the potential and not so much from a difference in the orbitals can be seen by considering the expectation values of the HF operator with the KS orbitals which are also given in Table V. They are quite close to the HF orbital energies.

TABLE V. OEPx and HF orbital energies in a.u. for N₂. The corresponding expectation values $\langle\hat{F}^{\text{HF}}\rangle$ of the KS orbitals with the HF operator \hat{F}^{HF} are also shown. The designation of the orbitals in the second column indicates the irreducible representation of the corresponding point group. λ_{\min} is the threshold for zero diagonal elements in the Cholesky decomposition.

Orbital	OEPx ^a	HF	$\langle\hat{F}^{\text{HF}}\rangle$
$1\sigma_g$	−14.3282	−15.6848	−15.6841
$1\sigma_u$	−14.3269	−15.6813	−15.6805
$2\sigma_g$	−1.3073	−1.4723	−1.4712
$2\sigma_u$	−0.7429	−0.7798	−0.7779
$1\pi_u$	−0.6636	−0.6142	−0.6153
$3\sigma_g$	−0.6329	−0.6348	−0.6329

^a $\lambda_{\min} = 10^{-5}$.

IV. CONCLUSION

It has been demonstrated that accurate OEP calculations for molecules can be performed without expanding the local potential in an auxiliary basis set. Choosing the orbital products $\psi_a\psi_i$ as expansion functions g_k for the potential, the buildup of the metric matrix **M** containing integrals $(\psi_b\psi_j|\psi_a\psi_i)$ [see Eq. (25)] requires a transformation of the electron repulsion integrals from the AO to the MO basis, which formally scales as N^5 if N is the number of AO basis functions. If an auxiliary basis set is used, the construction of the matrix **M** as given by Eq. (25) scales as N^4 because the dimension of the auxiliary basis grows only linearly with the system size in contrast to the quadratic increase of the number of orbital products $\psi_a\psi_i$. The less favorable scaling behavior of the present method is not necessarily prohibitive with respect to practical applications because the OEP method can make full use of its potential only after the development of appropriate orbital-dependent correlation functionals. The scaling of which is as yet unknown. Note that perturbation expansions based on the KS determinant as a reference⁴² lead to correlation energies of the same type as the second-order Møller-Plesset expression which also results in formal N^5 scaling. The most important step in the present method is the selection of a linearly independent subset from the complete set of orbital products $\psi_a\psi_i$ by a Cholesky decomposition accompanied by a reordering of the basis functions in each iteration step as described by Beebe and Linderberg.³⁵ This avoids the unfavorable N^6 scaling which would arise if the singular value decomposition according to Eq. (31) had to be performed for the matrix representation of the response function with the complete set of orbital products.

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APPENDIX: CHOLESKY PROCEDURE FOR THE ELIMINATION OF LINEARLY DEPENDENT VECTORS

A procedure developed by Beebe and Linderberg³⁵ for selecting a linearly independent set of functions out of a

linearly dependent set, in such a way that the reduced set still spans the same space as the original set, will be described. Denoting this set as $\{\Omega_i\}$, the scalar products $M_{ij} = (\Omega_i|\Omega_j)$ form the metric of this vector space. The metric matrix \mathbf{M} is singular if the set $\{\Omega_i\}$ is linearly dependent. The method of choice for the inversion of a square symmetric matrix is the Cholesky decomposition according to which the matrix \mathbf{M} is decomposed into a product of a lower triangular matrix and its adjoint,

$$\mathbf{M} = \mathbf{L}\mathbf{L}^\dagger. \quad (\text{A1})$$

From the definition [Eq. (A1)], we obtain the following relationships:

$$L_{kk} = \sqrt{M_{kk} - \sum_{j=1}^{k-1} L_{kj}^2}, \quad (\text{A2})$$

$$L_{ik} = \frac{M_{ik} - \sum_{j=1}^{k-1} L_{ij}L_{kj}}{L_{kk}} \quad i > k,$$

which lead to an iterative procedure for the construction of \mathbf{L} , with the matrix elements in the k th iteration step being updated as follows:

$$L_{kk} = \sqrt{M_{kk}^{(k-1)}},$$

$$L_{ik} = \frac{M_{ik}^{(k-1)}}{L_{kk}} \quad i > k, \quad (\text{A3})$$

$$M_{ij}^{(k)} = M_{ij}^{(k-1)} - L_{ik}L_{jk} \quad i \geq j > k.$$

It can be seen from Eq. (A3) that this procedure no longer works if there are vanishing diagonal elements L_{kk} . This is just the case for a linearly dependent basis $\{\Omega_i\}$ as can be shown most easily by pointing to a close relationship between the Cholesky decomposition and the Schmidt orthogonalization procedure, with the orthogonalized vectors χ_i being obtained as

$$\chi_i = \Omega_i - \sum_{k=1}^{i-1} \chi_k \frac{(\chi_k|\Omega_i)}{(\chi_k|\chi_k)}. \quad (\text{A4})$$

Using

$$(\chi_i|\Omega_i) = (\chi_i|\chi_i), \quad (\text{A5})$$

Eq. (A4) can be rewritten as

$$\Omega_i = \sum_{k=1}^i \chi_k \frac{(\chi_k|\Omega_i)}{(\chi_k|\chi_k)}. \quad (\text{A6})$$

Using Eq. (A6) and taking into account the orthogonality of the vectors χ_k , the matrix elements of the metric are obtained as

$$M_{ij} = (\Omega_i|\Omega_j) = \sum_{k=1}^{\min(i,j)} \frac{(\Omega_i|\chi_k)}{(\chi_k|\chi_k)^{1/2}} \frac{(\chi_k|\Omega_j)}{(\chi_k|\chi_k)^{1/2}}. \quad (\text{A7})$$

Comparison of Eqs. (A1) and (A7) immediately gives

$$L_{ik} = \frac{(\Omega_i|\chi_k)}{(\chi_k|\chi_k)^{1/2}}. \quad (\text{A8})$$

Forming the squared norm of the vectors [Eq. (A4)] and taking into account Eq. (A8), a comparison with Eq. (A2) leads to a relationship between the norm of the Schmidt orthogonalized vectors and the diagonal elements of the matrix \mathbf{L} ,

$$(\chi_k|\chi_k) = L_{kk}^2. \quad (\text{A9})$$

In the course of a Schmidt orthogonalization, a linear dependence is encountered if the norm of a vector χ_i , i.e., L_{ii} is zero indicating that this vector, does not have any component outside the vector space spanned by the previously orthogonalized vectors χ_k , with $k < i$ so that the basis vector Ω_i can be represented as a linear combination of these vectors and should therefore be discarded. In practical calculations, this is the case if the corresponding matrix element L_{ii} falls below a predefined threshold. To perform this elimination of linearly dependent vectors in a systematic fashion, the basis vectors should be reordered in each iteration step of the Cholesky decomposition such that the linear dependent vectors are shifted upward in the course of the iteration, so that they finally correspond to the highest indices. One proceeds as follows: before the k th iteration step, as shown in Eqs. (A3), the rows and columns of the matrix are rearranged for all indices $i \geq k$ in such a way that the diagonal elements appear in decreasing order. This guarantees that the diagonal elements of the final matrix \mathbf{L} are also arranged in decreasing order at the end of the iteration procedure, because the diagonal elements can only get smaller in the course of the iteration as can be seen from Eq. (A3). If the current diagonal element falls below some specified threshold in the k th iteration step, the Cholesky decomposition is stopped and the remaining basis vectors for $i \geq k$ are discarded from the set of functions $\{\Omega_i\}$. They form the nullspace because they are just linear combinations of the previous vectors. Following this procedure, the maximum number of iteration cycles according to Eqs. (A3) corresponds to the number of linearly independent functions, which can be much smaller than the dimension of the basis in case of a highly singular matrix \mathbf{M} .

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